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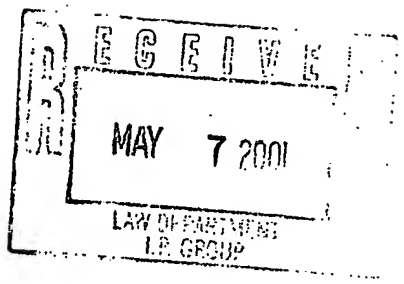

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COLORANT COMPOSITIONS

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Claims

1. Finely powdered colorant compositions for thermoplastic resins comprising 10-90 parts by weight of high-density polyethylene wax prepared by high-pressure radical polymerization and having a number-average molecular weight of 2000-8000, melting point of 100-130°C, and density of 0.93-0.97 g/cm^2 and [sic; cm^3] 90-10 parts by weight of pigments or oil-soluble dyes.

2. The colorant compositions according to Claim 1 wherein the thermoplastic resins are polyamide resin, polyethylene terephthalate resin, polyoxymethylene resin, and polyphenylene ether resin.

Detailed explanation of the invention

Industrial application field

The present invention relates to colorant compositions for thermoplastic resins. More specifically, the present invention relates to finely powdered colorant compositions with good adhesion to resin pellets, as well as good dispersion property and color stability. Also, they do not scatter, even with high pigment or dye content, when used in thermoplastic resins.

Prior art

Various kinds of colorants can be used for coloration of thermoplastic resins, and various colorants such as the raw pigment type, dry color type, masterbatch type, master powder type, etc. are used in practice.

Problems to be solved by the invention

Raw pigment type colorants scatter excessively and contaminate equipment. They cannot form sufficiently homogeneous dispersions, which causes the external appearance as well as the physical properties to be inferior.

Dry color type colorants are obtained by simply mixing dyes or pigments with metallic soap, wax, inorganic powder, etc., and thus there is a difficulty in their application to uses requiring high dispersion. Further, they also have the drawback of contaminating the environment due to a large scattering characteristic. Masterbatch type colorants are obtained by kneading dyes or pigments with synthetic thermoplastic resins. These colorants have the drawbacks of the synthetic thermoplastic resins available for coloring being limited and the properties of the synthetic thermoplastic resins degrading after coloring.

Conventional master powder type colorants are manufactured, for example, by kneading and dispersing dyes or pigments in low-density polyethylene wax and pulverizing. However, if a known pulverizer such as an atomizer is used for pulverization in the above case, gelation occurs in the pulverizer, making it difficult to obtain a fine powder; a specific pulverizer such as a freezing pulverizer, etc. must be used. In addition, when the content of dyes or pigments is increased greatly in order to improve the grinding property, the problem of dispersion arises during molding.

As explained above, currently known colorants cannot be used in a wide range of areas due to specific drawbacks.

Means to solve the problems

In consideration of the aforementioned drawbacks, the present inventors assiduously conducted research to obtain colorants that exhibit satisfactory adhesion to resin pellets in addition to good dispersion, color stability, and color mixing that can be easily pulverized, do not scatter even with high pigment or dye contents, do not deteriorate the physical property of molded materials, are easy to handle and have wide applicability. As a result, it was found that finely powdered colorants which do not have the aforementioned drawbacks are obtained by homogeneously mixing and dispersing compositions comprising 10-90 parts by weight of high-density polyethylene wax prepared by high-pressure radical polymerization and having a number-average molecular weight of 2000-8000, melting point of 100-130°C, and density of 0.93-0.97 g/cm^2 and 90-10 parts by weight of pigments or oil-soluble dyes under heating and by finely pulverizing the compositions. The present invention was thus completed.

All pigments or oil-soluble dyes appropriate for coloration of synthetic thermoplastic resins can be used in the present invention. As organic pigments, monoazo type, polyazo type, phthalocyanine type, quinacridone type, and other heterocyclic types are exemplified. As inorganic pigments, carbon black, titanium oxide, iron red oxide, navy blue, chrome yellow, barium sulfate, calcined pigments, etc. are exemplified. As the oil-soluble dyes, monoazo type, disazo type, anthraquinone type, perinone type, and other heterocyclic types are exemplified. The aforementioned pigments or oil-soluble dyes are selected as suitable according to their application purpose such as light resistance, weather resistance, heat resistance, chemical resistance, resistance to shifting, etc.

The polyethylene wax to be used in the present invention is high-density polyethylene wax prepared by high-pressure radical polymerization and having a number-average molecular weight of 2000-8000, melting point of 100-130°C, and density of 0.93-0.97 g/cm^2, preferably number-average molecular weight of 3000-6000, melting point of 105-125°C, and density 0.94-0.96 g/cm^2.

It is especially important for the polyethylene wax used in the present invention to be manufactured by a high-pressure radical polymerization process. The purpose of the present invention cannot be achieved by using the polyethylene wax prepared by other methods, e.g., polyethylene decomposition method, medium- or low-pressure anion polymerization method, etc.

With regard to the polyethylene wax, if the number-average molecular weight is less than 2000, or the density is less than 0.93 g/cm^2, or the melting point is lower than 105°C, fine pulverization at normal temperature in an atomizer, etc. is difficult. In addition, when the number-average molecular weight exceeds 8000, sometimes the effectiveness of the polyethylene wax is damaged and the characteristics of synthetic thermoplastic resins degrade after coloring. In addition, when the melting point is higher than 130°C, processors that can be used for kneading the colorant compositions are restricted, and it is difficult to disperse pigments or oil-soluble dyes.

In the colorant compositions of the present invention, the mixing ratio of pigments or oil-soluble dyes to high-density polyethylene wax prepared by high-pressure polymerization is 10-90 parts by weight to 90-10 parts by weight. When the mixing ratio of pigments or oil-soluble dyes is lower than the aforementioned lower limit, it is difficult to finely pulverize at normal temperature in an atomizer, etc.; on the other hand, when it is higher than the upper limit, the fluidity during kneading under heating is lowered, sometimes causing poor dispersion of pigments or oil-soluble dyes. The mixing ratio is preferably 30-85 parts by weight to 70-15 parts by weight.

The colorant compositions of the present invention contain the aforementioned two components as indispensable ingredients, but if necessary, fillers such as calcium carbonate, clay, talc, etc., as well as antioxidants, UV absorbents, etc. can be added.

The colorant compositions of the present invention can be manufactured, for example, by kneading ingredients in entirety under heating in a kneading machine such as a three-roll mill, kneader, Banbury mixer, etc., cooling to normal temperature, and pulverizing using a known pulverizer, e.g., an atomizer provided with a 1 mm-diameter screen.

The thermoplastic resins to be colored by the colorant compositions of the present invention are mainly engineering plastics, and, for example, polyamide resin (e.g., nylon 6, 66, 610, 11, 12, 46, etc.), polybutylene terephthalate resin, polyethylene terephthalate resin, polyoxymethylene resin, polyphenylene ether resin, and their mutual blends are preferred.

Effect of the invention

In recent years, the use of the aforementioned engineering plastics has expanded due to their excellent mechanical properties and heat resistance, and in keeping with this trend the need

of coloration is also raised. But, in various conventional kinds of colorants, sufficient dispersion and diffusion cannot be obtained, or the mechanical property is damaged further for the masterbatch type, colorants must be prepared for each resin and thus they are deficient due to their general nature.

The colorant compositions of the present invention solve the aforementioned various problems, have excellent effects such as satisfactory adhesion to resin pellets, dispersion, color stability, and color mixing without scattering, even with high pigment or dye contents, and can be used for a wide range of resins.

Application examples

Next, the present invention is explained in detail with application examples, but the present invention is not limited to them only. Furthermore, "parts" used in application examples and comparative examples means "parts by weight."

Application Example 1

50 parts copper phthalocyanine blue, 50 parts polyethylene wax (AH-6 wax, BASF, molecular weight 6000, melting point 115-122°C, density 0.94-0.96 g/cm^2, high-density type), and 0.1 part antioxidant (Sumilizer BP101) were mixed, kneaded under heating in a three-roll mill, cooled, and pulverized in a pulverizer (atomizer) provided with a 1 mm-diameter screen to obtain a finely powdered colorant composition of 32 mesh. When 10 parts of the composition were mixed with 500 parts of polybutylene terephthalate resin pellets (Toray PBT1400L) in a small blender the adhesion to the resin was satisfactory. Then, the mixture was directly molded by an injection molding machine to obtain a uniformly colored plate with satisfactory dispersion.

Application Example 2

A finely powdered colorant composition was obtained by the same manner as in Application Example 1 except that AH-3 wax, BASF (molecular weight 3000, melting point 105-112°C, density 0.94-0.95 g/cm^2, high-density polyethylene wax), instead of AH-6 wax, BASF, was used. When 10 parts of the composition were mixed with 500 parts of nylon resin pellets (Unitika Nylon A1030BRL) in a small blender, the adhesion to the resin was satisfactory. Then, the mixture was directly molded by an injection molding machine to obtain a uniformly colored plate with satisfactory dispersion.

Comparative Example 1

A finely powdered colorant composition was obtained by the same manner as in Application Example 1 except that Hi-Wax 600P (polyethylene wax prepared by medium- and

low-pressure anion polymerization method, molecular weight 5700, melting point 139°C, density 0.97 g/cm^2, high density type, from Mitsui Petrochemical Industry Co.), instead of AH-6 wax, BASF, was used. When it was molded by the same manner as in Application Example 1 to a plate, the dispersion was poor, and the plate had only 70% coloration as compared with the plate obtained in Application Example 1.

Application Example 3

40 parts carbon black, 30 parts AH-6 wax, BASF, 30 parts AH-3 wax, BASF, and 0.1 part Sumilizer BP101 were mixed, kneaded under heating in Banbury mixer, cooled, and treated by the same manner as in Application Example 1 to obtain a finely powdered colorant composition. The composition was molded by the same manner as in Application Example 1 to obtain a uniformly colored plate with satisfactory dispersion.

Application Example 4

80 parts titanium oxide, 20 parts AH-6 wax, BASF, and 0.1 part Sumilizer BP101 were mixed, kneaded under heating in a kneader, cooled, and treated by the same manner as in Application Example 1 to obtain a finely powdered colorant composition. The composition was molded by the same manner as in Application Example 1 to obtain a uniformly colored plate with satisfactory dispersion.

Application Example 5

85 parts titanium yellow, 15 parts AH-6 wax, BASF, and 0.1 part Sumilizer BP101 were mixed and treated by the same manner as in Application Example 1 to obtain a finely powdered colorant composition. The composition was molded by the same manner as in Application Example 1 to obtain a uniformly colored plate with satisfactory dispersion.

Comparative Example 2

The same operation as in Application Example 1 was carried out using the same composition as in Application Example 5 except that A wax, BASF (polyethylene wax obtained by high-pressure radical polymerization, molecular weight 5000, melting point 97-103°C, density 0.91-0.93 g/cm^2, low density type), instead of AH-6 wax, BASF, was used, but the composition gelled in the pulverizer and thus a finely powdered colorant composition could not be obtained.

Comparative Example 3

The same operation as in Application Example 1 was carried out using the same composition as in Application Example 5 except that Sanwax 165P (polyethylene wax obtained by the polyethylene decomposition method, molecular weight 5000, melting point 107°C, density 0.91 g/cm^2, low density type, from Sanyo Kasei Co.), instead of AH-6 wax, BASF, was used, but the composition gelled in the pulverizer and thus a finely powdered colorant composition could not be obtained.

Application Example 6

5000 parts of nylon resin pellets (Unitika Nylon A1030BRL), 10 parts of the colorant composition (blue composition) obtained in Application Example 1, 5 parts of the colorant composition (black composition) obtained in Application Example 3, 75 parts of the colorant composition (white composition) obtained in Application Example 4, and 10 parts of the colorant composition (yellow composition) obtained in Application Example 5, were mixed in supermixer, and the mixture was (1) directly injection molded to a plate, (2) injection molded to a plate after color compounding in a single-screw extruder, and (3) injection molded to a plate after color compounding in a twin-screw extruder. When three colored plates of (1)-(3) were compared, no difference in hue was confirmed, and all of the plates were uniformly colored gray and had satisfactory color mixing and color stability.

Comparative Example 4

5000 parts nylon resin pellets (Unitika Nylon A1030BRL) were mixed with, as dry colors (pigments and metallic soap were processed in an atomizer) having the composition shown in Table 1, 10 parts blue, 5 parts black, 75 parts white, and 10 parts yellow in a supermixer and molded by the same manner as in Application Example 6 to obtain three colored plates of (1)-(3). When compared, the dispersion was poor, and there was a large difference in hue.

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⑭発明の名称　着色剤組成物

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明　細　書

1．発明の名称

着色剤組成物

2．特許請求の範囲

(1)高圧ラジカル重合法により得られた数平均分子量2000～8000、融点100～130℃、密度0.93～0.97g/cm³の高密度ポリエチレンワックス10～90重量部に対して、顔料または油溶性染料90～10重量部を配合してなる微粉末状の熱可塑性合成樹脂用着色剤組成物。

(2)熱可塑性合成樹脂がポリアミド樹脂、ポリブチレンテレフタレート樹脂、ポリエチレンテレフタレート樹脂、ポリオキシメチレン樹脂、ポリフェニレンエーテル樹脂などである特許請求の範囲第一項記載の組成物。

3．発明の詳細な説明

〈産業上の利用分野〉

本発明は熱可塑性合成樹脂用着色剤組成物に関するものである。更に詳しくは本発明は高い染顔料含有量の場合であっても飛散性がなく、ペレット樹脂への付着性、分散性、発色安定性、混色性が良好な微粉末状の熱可塑性合成樹脂用着色剤組成物に関するものである。

〈従来の技術〉

熱可塑性合成樹脂の着色に使用される着色剤には種々のタイプがあり、例えば生顔料タイプ、ドライカラータイプ、マスターバッチタイプ、マスターパウダータイプ等の各種の着色剤が実用に供されている。

〈発明が解決しようとする課題〉

生顔料タイプの着色剤は、飛散性、機器汚染が強く、また分散の均一性に欠け、外観不良、物性不良の原因となる。

ドライカラータイプの着色剤は、染顔料を金属石けん類、ワックス類、無機質の粉末等と単に混合したものであり、高度の分散を要求される用途には難点があり、飛散性が大きいので周囲を汚染する欠点もある。　マスターバッチタイプの着色剤は、染顔料を熱可塑性合成樹脂に混練りしたものであり、着色される熱可塑性合成樹脂が限定さ

れたり、着色される熱可塑性合成樹脂の特性が減ぜられるという欠点がある。

従来のマスターパウダータイプの着色剤は、例えば、染顔料を低密度ポリエチレンワックスに混練り分散させた後、これを粉砕させて製造されている。しかし、この場合には粉砕に際して、公知の粉砕機、例えば、アトマイザーを使用すると粉砕機内部でゲル化を起こし微粉末になりにくく、冷凍粉砕機等の特殊な粉砕機を使用しなければならない。また、粉砕性を良くするために、染顔料含有量を低減に高くした場合には、成形時の分散性に問題があった。

上述の如く現在知られている着色剤は夫々の欠点のために広い用途範囲に使用できなかった。

〈課題を解決するための手段〉

本発明者らは上述の欠点に鑑み、熱可塑性合成樹脂の着色に於いて高い染顔料含有量であっても、容易に微粉砕可能であって飛散性がなく、ペレット樹脂への付着性、分散性、発色安定性、混色性が良好で、成形加工時における加工性を悪化させず、成形物の物性を低下させず、取り扱いが便利で汎用性のある着色剤を得るべく鋭意検討した結果、高圧ラジカル重合法により得られた数平均分子量２０００～８０００、融点１００～１３０℃、密度０．９３～０．９７g/cm³ の高密度ポリエチレンワックス１０～９０重量部に対して、顔料または油溶性染料９０～１０重量部を配合してなる組成物を、加熱下に於いて均一に混合分散し常温で微粉砕でき、かつ前述の欠点を有しない微粉末状着色剤が得られることを見い出し本発明を完成するに至った。

本発明で使用される顔料または油溶性染料とは、熱可塑性合成樹脂の着色に供せられる適性を有するものであれば、すべて良好に使用できる。例えば有機顔料としては、モノアゾ系、ポリアゾ系、フタロシアニン系、キナクリドン系、その他複素環系などがあげられ、無機顔料としては、カーボンブラック、酸化チタン、弁柄、群青、黄鉛、硫酸バリウム、焼成顔料などがあげられる。油溶性染料としては、モノアゾ系、ジスアゾ系、アンスラキノン系、ペリノン系、その他複素環系などがあげられる。上記の顔料または油溶性染料は、耐光性、耐候性、耐熱性、耐薬品性、耐移行性などの使用目的に応じ適性を選定の上使用される。

本発明で使用されるポリエチレンワックスとは、高圧ラジカル重合法により得られた数平均分子量２０００～８０００、融点１００～１３０℃、密度０．９３～０．９７g/cm³ 、好ましくは数平均分子量３０００～６０００、融点１０５～１２５℃、密度０．９４～０．９６g/cm³ の高密度ポリエチレンワックスである。

本発明に使用されるポリエチレンワックスは、高圧ラジカル重合法で製造される事が特に重要であり、他の製造方法例えば、ポリエチレン分解法や中・低圧アニオン重合法のポリエチレンワックスを用いては、本発明の目的が達せられない。

このポリエチレンワックスにおいて、数平均分子量が２０００未満または密度０．９３g/cm³ 未満または融点１０５℃未満であれば、アトマイザー等での常温での微粉砕が困難である。また、数平均分子量が８０００を越えると、ポリエチレンワックスとしての性能が損なわれ着色される熱可塑性合成樹脂の特性が減ぜられる場合があり、また融点が１３０℃より高くと着色剤組成物を混練りする際の加工機に制約を受けたり、顔料または油溶性染料の分散が困難となる。

本発明の着色剤組成物における顔料または油溶性染料と高圧ラジカル重合法により得られた高密度ポリエチレンワックスの重量配合割合は１０～９０重量部：９０～１０重量部である。顔料または油溶性染料の重量配合割合が、上記下限値より少ないとアトマイザー等での常温での微粉砕が困難となり、上記上限値より多いと、加熱混練り時に流動性が低下、顔料または油溶性染料の分散不良の原因となる場合があり、好ましくは３０～８５重量部：７０～１５重量部である。

本発明の着色剤組成物は前記二成分を必須成分とするものであるが、さらに必要に応じて、炭酸カルシウム、クレー、タルク等の充てん剤、酸化防止剤、紫外線吸収剤などを添加することもでき

る。

本発明の着色剤組成物は、例えば、全成分を三本ロールミル、ニーダー、バンバリーミキサーなどの混練り機で加熱混練り後、常温まで冷却し、公知の粉砕機、例えば直径1㎜のスクリーンをつけたアトマイザーで粉砕することにより容易に製造することが出来る。

本発明による着色剤組成物によって着色される熱可塑性合成樹脂としては、主としてエンジニアリングプラスチックスであり、例えば、ポリアミド樹脂（例えばナイロン6、66、610、11、12、46等）、ポリブチレンテレフタレート樹脂、ポリエチレンテレフタレート樹脂、ポリオキシメチレン樹脂、ポリフェニレンエーテル樹脂等及びこれらの相互のブレンド物などが好ましい。

＜発明の効果＞

上記のエンジニアリングプラスチックスは、機械物性、耐熱性が優れているため近年用途が拡大し、それに伴って着色のニーズも高いが従来の種々の着色剤タイプでは充分な分散、拡散性が得られなかったり、機械物性を損なうことがあり、またマスターバッチタイプは着色剤を樹脂別に作らなければならず汎用性が乏しかった。

本発明の着色剤組成物は前述の種々の問題を解決し、高い染顔料含有量での場合でも飛散性がなく、ペレット樹脂への付着性、分散性、発色安定性、混色性が良好であるという優れた効果を示し広範囲の樹脂に広く使用することが出来る。

＜実施例＞

以下実施例により本発明を具体的に説明するが本発明はこれらの実施例により何ら限定されるものではない。なお、実施例及び比較例中の部は重量部を表す。

実施例1

銅フタロシアニンブルー50部、ポリエチレンワックス（AH－6ワックスBASF、分子量6000、融点115～122℃、密度0.94～0.96g/cm²、高密度タイプ）50部、及び酸化防止剤（スミライザーBP101）0.1部を混合し、三本ロールミルで加熱混練りした後冷却し、直径1㎜のスクリーンをつけた微粉砕機（アトマイザー）を用い常温で粉砕を行い、32メッシュ通過の微粉末着色剤組成物を得た。得られた組成物10部、ポリブチレンテレフタレート樹脂ペレット（東レPBT1400L）500部を小型ブレンダーにて混合したところ、樹脂への付着性が良好で直接射出成形機にてプレートに成形したところ、分散性が良好で均一に着色された成形物が得られた。

実施例2

実施例1に於いてAH－6ワックスBASFの代わりにAH－3ワックスBASF（分子量3000、融点105～112℃、密度0.94～0.95g/cm²、高密度タイプによるポリエチレンワックス）に変えた以外は実施例1と同様にして微粉末着色剤組成物を得た。得られた組成物10部、ナイロン樹脂ペレット（ユニチカナイロンA1030BRL）500部を小型ブレンダーにて混合したところ、樹脂への付着性が良好で直接射出成形機にてプレートに成形したところ、分散性が良好で均一に着色された成形物が得られた。

比較例1

実施例1に於いてAH－6ワックスBASFの代わりに三井石油化学製ハイワックス600P（中・低圧アニオン重合法によるポリエチレンワックス、分子量5700、融点139℃、密度0.97g/cm²、高密度タイプ）に変えた以外は実施例1と同様にして微粉末着色剤組成物を得た。得られた組成物を実施例1と同様にしてプレートに成形したところ、分散性が悪く実施例1で得られたプレートに比較して、70％の着色力のものしか得られなかった。

実施例3

カーボンブラック40部、AH－6ワックスBASF30部、AH－3ワックスBASF30部、及びスミライザーBP101　0.1部を混合し、バンバリーミキサーで加熱混練りした後冷却し、実施例1と同様にして微粉末着色剤組成物を